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Evaluation of a fibrous cellulose drying agent in supercritical fluid extraction and pressurized liquid extraction of diverse pesticides

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Abstract

A fibrous cellulose powder (CF-1) was investigated as a drying agent for supercritical fluid extraction (SFE) and pressurized liquid extraction (PLE), also known as accelerated solvent extraction. Analysis of fifty-eight diverse pesticides was performed using gas chromatography–ion-trap mass spectrometric detection (GC–ITD). Extraction efficiencies were correlated versus pesticide polarity with samples of different water–CF-1 ratios. The effect of water was much more pronounced in SFE using CO_2 than PLE using acetonitrile. Pesticide recoveries and limits of detection of fortified tomato samples mixed with CF-1 were determined. PLE gave recoveries >80% for nearly all pesticides, and SFE gave similar recoveries except for the most polar and non-polar pesticides. SFE typically gave lower detection limits than PLE due to fewer matrix interferants. © 1997 Elsevier Science B.V.

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1. Introduction

Multiresidue analysis of pesticides in food is performed routinely in regulatory and industrial laboratories around the world. Many current methods of multiresidue analysis are labor-intensive, time-consuming and generate hazardous waste [1]. Due to economic, environmental and other concerns, many laboratories must consider the use of faster, more automated and less wasteful methods. Pressurized liquid extraction (PLE) and supercritical fluid extraction (SFE) are two automated bench-top instrumental techniques that can achieve these goals.

PLE is also known by the trade names Accelerated Solvent extraction (ASE) or Enhanced Solvent Extraction (ESE), and by another generic term, pressurized fluid extraction. The latter term does not distinguish between SFE and PLE, which both involve pressurized fluids, thus PLE will be used in this article. Alternative terms that use "solvent" in the description also do not distinguish between SFE and PLE, and allusions to temperature in the term are not appropriate because application of heat is not a prerequisite in this form of extraction.

The principles of both SFE and PLE techniques are similar in that pressure and temperature are controlled in the extraction process. The greatest difference is that PLE uses liquid solvents and SFE uses a supercritical fluid (typically CO_2) for extraction. PLE takes advantage of the increased analyte solubility and extraction kinetics at higher temperature to speed the extraction process and reduce solvent consumption [2] versus traditional methods. Pressure has less influence on analyte

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Table 1
Parameters of the PLE and SFE instruments used in the study

Parameter	PLE	SFE
Temperature (°C)	25, 40–200	25–150
Pressure (p.s.i.)	1000–3000	1100–5578
Extraction vessel sizes (ml)	11, 22, 33	7
Flow-rate (ml/min)	≈8	≤4
Collection vial sizes (ml)	40, 60	1.8
Trapping	None	Solid sorbent

recoveries than temperature in PLE, but elevated pressure: (1) maintains the solvent in the liquid state at high temperatures; (2) may help the solvent enter small pores in the sample; and (3) forces flow through the sample and filter during the short dynamic mode. In SFE, pressure and temperature each alter supercritical fluid density, and alterations in either parameter can affect the extraction process significantly. Due to the wide range of fluid densities and solvent modifiers in SFE, a higher degree of selectivity is often possible with SFE than with liquid-based extractions, but SFE using CO_2 can have difficulties in extraction of polar compounds. In multiresidue analysis, the variety of pesticides to be extracted often limits the extent of selectivity that can be achieved.

The designs of current commercial PLE and SFE instruments are similar in many ways (reduced sample size, automated sequential extraction of samples loaded into vessels, static and dynamic extraction and comparable temperature ranges). Table 1 compares parameters of SFE and PLE for the instruments used in this study.

In the case of samples with high water content, a key aspect of either approach is the use of a drying agent to control water and to disperse the sample. Furthermore, a more homogeneous sample, for subsampling in SFE and PLE, can be prepared with a drying agent for fruits and vegetables [3] than simply blending the sample (water separates from the pulp).

The ideal drying agent has the following characteristics: (1) high water retention capacity, (2) good sample consistency, (3) high density for packing vessels, (4) low cost, (5) does not retain analytes, (6) does not heat during hydration and (7) causes no interferences in analysis. Furthermore, the material should be non-hazardous and be able to withstand high pressure and temperature.

Burford, et al. [4] compared drying agents for SFE of environmental pollutants in soil and sludge applications, and this laboratory compared Hydromatrix, Celite, and salt desiccants for multiresidue applications in produce [5]. Table 2 lists some of the qualities of selected drying agents. One must exercise caution when using certain drying agents, such as sodium sulfate, which appears to be a good choice based on Table 2. In practice, sodium sulfate has slower kinetics for complete hydration than the other materials, and the decahydrate melts at 32.4°C [6] which can cause clogs in SFE and PLE. The relatively weak water retention capabilities and high solubility in water are other factors to consider with $MgSO_4$ and Na_2SO_4 [6]. Molecular sieves retain water better, but have a relatively low capacity. Celite and Hydromatrix are the most common drying agents in SFE, but they retain polar pesticides, such as methamidophos, acephate, and omethoate [7,8]. $MgSO_4$ and other salts allow for higher recovery of

Table 2
Comparison of selected drying agents

Drying agent	Saturation ratio (water–drying agent)	Cost (cents/g)	Heat of hydration	Density (g/ml)[3]	Consistency
Celite 545	3:1[1]	1.2	None	0.36	Compact
Hydromatrix	3:1[1]	3.8	None	0.29	Pelletized
Cellulose, CF-1	4:1[1]	5.0	None	0.21	Fluffy
Molecular sieves[4]	0.5:1[1]	4.0	Moderate	0.83	Variable
Magnesium sulfate	1.05:1[2]	5.0	High	0.62	Powdery
Sodium sulfate	1.27:1[2]	2.2	Low	1.4	Grainy

[1] Determined by addition of water at room temperature.
[2] Determined by calculation using molecular masses.
[3] Amount of dry material packed in an extraction vessel divided by volume.
[4] Molecular sieves 5A ground with mortar and pestle.

polar pesticides [9], but recovery of the non-polars appear to be reduced in real samples [5].

Pesticides spiked on filter paper indicated that polar pesticides may not be retained by cellulose in SFE [5]. A major objective of this study was to investigate a previously untested drying agent, fibrous cellulose powder, and determine if both polar and non-polar pesticides could be extracted from the fibrous cellulose in a single SFE procedure. A second objective was to determine the optimal sample–cellulose ratio in SFE and PLE. Also, this study presented an opportunity to compare SFE and PLE results in the analysis of multiple pesticides in tomato mixed with fibrous cellulose.

2. Experimental

2.1. Chemicals

CF-1, fibrous cellulose powder, manufactured by Whatman (Maidstone, UK) was used as the drying agent in this study. The fibrous cellulose, prepared by the manufacturer from cotton, consisted of 99% alpha cellulose and contains numerous hydroxyl groups. For comparison purposes, two portions of CF-1 were used: one portion was unwashed and sieved to remove particles <105 μm (140 mesh), and the other portion was washed with methylene chloride, decanted to remove fines and dried in an oven. Water was obtained from a Barnstead filtration system. All solvents used were pesticide-grade, and sodium chloride and anhydrous sodium sulfate were ACS-certified grade. CO_2 in SFE was 99.9999% purity for extraction (Air Products, Hyattsville, MD, USA) and bone-dry grade CO_2 was used for cooling the trap and pump heads. The PLE used 99.998% purity nitrogen for purging the vessels after extraction, and for instrument pneumatics. The same grade of N_2 was also used for solvent evaporation. Helium (99.999%), passed through an in-line water–O_2 trap, was the GC carrier gas. The pesticide standards used in this study were typically 99% or higher purity obtained from the US Environmental Protection Agency (Beltsville, MD, or Research Park, NC, USA). Pesticide stock solutions of 1000–10 000 μg/ml in acetone were prepared, and a mixture of fifty-eight pesticides was prepared in acetone from the stock solutions. Table 3 lists the pesticides and their concentrations in the spiking solution as well as other pertinent aspects of the pesticides. An internal standard solution of 20 μg/ml of anthracene-d10 and chrysene-d12 (Cambridge Isotope Laboratories, Woburn, MA, USA) was prepared in acetone, and an amount was added to all extracts to give an equivalent of 0.1 μg/g per sample.

2.2. Sample preparation

To determine the effect of water on pesticide recoveries, water was added to CF-1, washed and unwashed portions, in different ratios before being loaded in the SFE and PLE vessels. Experiments included dry CF-1 (containing 3% water according to product information), (1:1), (2:1), (3:1) and (4:1) water–CF-1 (w/w). The spiking solution was dispersed well in the matrix prior to loading the vessels. Independent of the amount of water, 1.5 g CF-1 was loaded in 7 ml SFE thimbles and 2 g CF-1 in 11 ml PLE vessels. Pesticide spiking levels were 10 μl per g CF-1 in SFE, and 100 μl per g CF-1 in PLE (see Table 3 for pesticide concentrations in spiking solution).

Tomatoes, labeled as being grown in greenhouses, were purchased at a local supermarket. The samples were chopped into small pieces with a knife and stored in closed containers in a freezer. Frozen 25 g portions of tomato were mixed in a blender or by hand with mortar and pestle. The spike solution, 10 μl/g tomato, was added to the tomato prior to mixing with CF-1. A small amount of dry ice (≈5 g) was added to the sample during mixing to maintain frozen conditions (samples were stored in the freezer and loaded in vessels while still frozen). For SFE, 4 g (2 g tomato) of (1:1) tomato–CF-1, and 4.5 g (3 g tomato) of (2:1) tomato–CF-1, were loaded into the 7 ml thimbles. A 1 cm disk (cut with a cork borer) of Whatman GF/F glass-fiber filter paper (0.7 μm pore size) was placed at each end of the samples to keep particles away from the thimble caps (flow was up). For PLE, 4 g (2 g tomato) of (1:1) tomato–CF-1, and 6 g (4 g tomato) of (2:1) tomato–CF-1, were loaded into the 11 ml vessels. A disk of Whatman D28 filter paper (1.9 μm pore size) was placed at the bottom of each vessel (flow was down).

Table 3
Information concerning the pesticides included in the study listed in order of retention time, t_r

Pesticide	Family	t_r (min)	Quantitation masses (u)	Standard concentration (μg–ml)	Solubility in water (mg/l)[1]
Dichlorvos (DDVP)	Organophosphate	6:28	109+185	10	$8–10·10^3$
Methamidophos	Organophosphate	6:40	141	100	$2·10^6$
Mevinphos	Organophosphate	9:22	192	10	$6·10^5$
Acephate	Organophosphate	9:44	136	300	$6.5–8.2·10^5$
Tetrahydrophthalimide	Phthalimide	10:46	151[2]	50	
Pentachlorobenzene	Organochlorine	11:08	248–252	5	Insoluble
o-Phenylphenol	Phenol	11:13	169+170	10	700
Omethoate	Organophosphate	12:52	156	100	Miscible
Propoxur	Carbamate	12:55	152	10	$1.9–2·10^3$
Diphenylamine	Phenylamine	13:18	167–169	5	
Chlorpropham	Carbamate	13:56	127+171+213	10	89
Trifluralin	Dinitroaniline	14:01	264+306	5	0.2–1
Phorate	Organophosphate	14:37	75+260	10	18–50
Hexachlorobenzene	Organochlorine	14:51	282–288	10	Insoluble
Dicloran (DCNA)	Nitroaniline	15:21	176+206	10	7
Dimethoate	Organophosphate	15:26	87+93	25	$2.38·10^4$
Carbofuran	Carbamate	15:36	164	15	350–700
Quintozene (PCNB)	Organochlorine	15:52	293–299	10	0.1–0.4
Atrazine	Triazine	15:53	215	10	33
Lindane (γ-HCH)	Organochlorine	16:06	183	40	6.6–7
Terbufos	Organophosphate	16:18	231	5	4–5
Diazinon	Organophosphate	16:37	137+179+304[3]	5	40–60
Chorothalonil	Organochlorine	16:48	266	25	0.6–1.2
Anthracene-d10	(I.S.)	16:51	188	–	
Disulfoton	Organophosphate	16:59	88+97+274	10	12–23
Phosphamidon	Organophosphate	18:11	127+264	25	$1·10^6$
Vinclozolin	Oxazolidine	18:36	212+285	10	2.6–3.4
Parathion-methyl	Organophosphate	18:42	263	10	55–60
Carbaryl	Carbamate	19:01	115+144	10	100
Malathion	Organophosphate	20:05	173	10	130–145
Chlorpyrifos	Organophosphate	20:18	314+316	10	0.7–1.2
Aldrin	Organochlorine	20:20	263+293	20	0.01–0.2
Dacthal (DCPA)	Organochlorine	20:28	299–303	10	0.5
Parathion	Organophosphate	21:38	291	10	24
Dichlorobenzophenone	Organochlorine	20:54	139+250	20	
Pendimethalin	Dinitroaniline	21:36	252	10	0.3
Captan	Phthalimide	22:19	79	70	3–5
Methidathion	Organophosphate	22:48	145	15	220
Thiabendazole	Benzimidazole	22:49	201	190	28–30
Disulfoton sulfone	Organophosphate	23:16	97+153[4]	15	
Endosulfan I	Organochlorine	23:20	241+267+339[6]	30	0.1–0.53
Fenamiphos	Organophosphate	23:48	260+288+303	50	330–700
Imazalil	Imidazole	24:13	173+215[5]	500	180–293
p,p'-DDE	Organochlorine	24:15	316+318	5	0.0012–0.14
Myclobutanil	Triazole	24:33	179	50	142
Endosulfan II	Organochlorine	25:39	241+267+339	30	0.1–0.53
Ethion	Organophosphate	25:55	231	5	1
o,p'-DDT	Organochlorine	25:57	235	15	0.001–0.04
Propargite	Sulfite ester	27:59	135+335+350	50	0.6–635
Iprodione	Imidazolidine	28:57	314+316	25	14
Phosmet	Organophosphate	29:08	160	10	20–25

Table 3 (*continued*)

Pesticide	Family	t_r (min)	Quantitation masses (u)	Standard concentration (μg–ml)	Solubility in water (mg/l)[1]
Chrysene-d_{12}	(I.S.)	29:17	240	–	
Methoxychlor	Organochlorine	29:29	227	15	0.1–0.12
Phosalone	Organophosphate	30:32	182	10	3–10
Azinphos methyl	Organophosphate	30:42	132	50	20–30
cis-Permethrin	Pyrethroid	33:28	183	10	0.006–0.2
trans-Permethrin	Pyrethroid	33:52	183	10	0.006–0.2
Cypermethrin	Pyrethroid	36:26	127+163+181	120	$1.9–4.1 \cdot 10^{-4}$
Fenvalerate	Pyrethroid	40:23	225+419	70	0.002–0.1
Esfenvalerate	Pyrethroid	41:31	225+419	70	0.002–0.1

[1] Values from Pesticide Properties Database (http://ncsr.arsusda.gov/ppdb3) at 20–25°C and pH 7.
[2–6]masses for SFE extracts; for PLE tomato extracts: [2]79, [3]304, [4]153+213, [5]173, [6]267+339.
I.S.=Internal standard.

2.3. Extraction

A Hewlett-Packard 7680T supercritical fluid extractor (Little Falls, DE, USA) was used for SFE. Extraction conditions were 350 bar and 50°C (CO_2 density=0.90 g/ml), 2 min equilibration time, 20.3 min dynamic time at 2 ml/min (6.0 thimble volumes of CO_2), and 50°C restrictor. Collection with an octyldecylsilane (ODS) trap was performed at 10°C, and elution was with 1.2 ml of acetone at 2 ml/min and 30°C. The trap was rinsed with 3 ml of additional acetone at 30°C and 2 ml/min before the next extraction. These conditions were determined from previous studies [8,10].

A Dionex ASE 200 extractor (Salt Lake City, UT, USA) was used for PLE. The extraction conditions were based on an existing multiresidue method (the clean-up step with celite–charcoal was not performed in this study) [11]. PLE conditions were: acetonitrile solvent, 2000 p.s.i. (1 p.s.i.=6894.76 Pa), 60°C, 5 min heat time, 2 min static time, 1 cycle of 100% flush volume (≈22 ml) and 60 s N_2 purge time. The extracts were collected in 40 ml vials capped with septa. After PLE, 1–2 g of NaCl (excess) was added to the extracts, and the upper acetonitrile layer was removed, shaken with Na_2SO_4, and evaporated to 2 ml volume under N_2 at 40°C. For the CF-1–water samples, the spiking level was higher and the evaporation step was not performed.

2.4. Analysis

Analysis was performed using a Finnigan ITS40 (San Jose, CA, USA) GC–ITD. Operating conditions for GC–ITD were: DB-5ms (J and W Scientific, Folsom, CA, USA), 30 m×0.25 mm I.D., 0.25 μm film thickness, capillary column, 5 m phenyl-methyl deactivated (Restek, Bellefonte, PA, USA) guard column (0.25 mm I.D.), 1 μl injection volume, Model 1093 (Varian, Walnut Creek, CA, USA) septum programmable injector (SPI); 50°C injection port for 6 s followed by ramping to 260°C at 20°C/min; 10 p.s.i. He column head pressure (34 cm/s at 50°C); 50°C initial oven temperature for 6 s, ramped to 130°C at 20°C/min, then to 260°C at 5°C/min, and held at 260°C until 43 min total time elapsed; 260°C transfer line temperature; and 220°C ion-trap manifold temperature. A modification of the SPI was made so that the septum purge flow was turned off during injection and on again 5 min later. ITD operating conditions were: electron impact mode, 12 μA filament current, 1500 V electron multiplier (K and M, West Springfield, MA, USA), and automatic gain control (AGC) at 30 000. The collection range was 74–420 m/z from 5–43 min for the analysis of the pesticides.

Quantitation masses were selected for each pesticide based on achieving the highest S/N value in tomato extract. Blank extracts were initially injected to determine possible matrix interferences, then they were fortified with the spiking solution to serve as calibration standards in matrix. The GC–ITD utilized Magnum version 2.4 software for data collection; peak areas were used for quantitation. Recoveries were calculated by dividing the pesticide peak area versus internal standard peak area of a spiked sample

by the signal versus internal standard responses of the calibration standards. Average limits of detection (LODs), concentration at $S/N=3$, for each pesticide was determined for each standard in matrix by multiplying the known concentrations (ng/g) by 3 and dividing by the S/N ratio (as reported by the GC–ITD software), and then multiplying the value by the pesticide recovery.

3. Results and discussion

3.1. Practical aspects of CF-1

The most prominent difference in using CF-1 versus other drying agents was the fluffy consistency of CF-1. When working with CF-1, it was easier to use a rod or mortar and pestle to mix the sample with CF-1 than a blender. Frozen conditions were maintained during sample preparation with dry ice, but the CF-1 still formed clumps with the sample which did not disperse easily in the blender. When the clumps were dispersed with a rod or mortar or pestle, the tomato–CF-1 mixture became homogeneous in color and consistency. Higher tomato–CF-1 ratio was easier to mix than a lower ratio, but the preparation of the homogenate was more difficult and time-consuming with CF-1 than with other drying agents in Table 2.

CF-1 washed with methylene chloride gave similar GC–ITD background spectra and pesticide recoveries as with unwashed CF-1. The washed CF-1 gave a slightly lower baseline in GC–ITD chromatograms than unwashed CF-1, and four minor contaminants were removed by the washing step, but the few matrix peaks that appeared in either case were relatively small and narrow. The washing step was unnecessary, but it did provide an easy way to remove fine particles from the CF-1. Small particles (≈2 μm) can clog frits and affect the restrictor in SFE. Sieving the CF-1 by hand is more laborious than decanting, but drying the material afterwards is more time consuming than sieving. Experiments with tomato used sieved, unwashed CF-1 to minimize consumption of organic solvents and save time.

CF-1 provided the highest water retention capacity of the drying agents listed in Table 2. The cost of the material was higher than other drying agents, but overall cost is reduced if less material can be used to absorb the same amount of water. Also, more sample can be packed into a vessel by using less drying agent. However, if water is not adequately retained, or if recoveries are affected by the higher water–CF-1 ratio, then the higher ratio cannot be used. Even with (4:1) water–CF-1, little water was removed from the CF-1 by SFE (elution volumes were consistent and the CF-1 was still wet after SFE). In PLE, the acetonitrile removed much of the water from the CF-1, but extract volumes were consistently ≈22 ml. The amount of water in the extracts increased with the water–CF-1 ratio, as observed in the salt partitioning step. Thus, CF-1 was able to retain water in SFE, but not in PLE with a solvent miscible with water.

3.2. Effect of water–CF-1 ratio

Water can play a critical role in SFE [12]. The addition of water to a dry matrix, in traditional methods as well, often improves recoveries of many pesticides. Water serves to swell the matrix to allow better fluid penetration, and to modify the polarity of the extraction fluid [13]. Despite its low solubility in supercritical CO_2, water is a strong modifier, and addition of other modifiers in the presence of water has not affected pesticide recoveries in food matrices [14]. In this study, the effect of water on the extraction of pesticides with a wide polarity range was studied to determine the optimal sample–CF-1 ratio in multiresidue extraction of fruits and vegetables, which contain 80–95% water.

Table 4 lists the SFE and PLE %recoveries and %R.S.D. of the pesticides when spiked on CF-1 and mixed with different amounts of water. The pesticides were divided into 5 categories (A–E) based on the trends of the results versus water content. The pesticides in each category were listed in order of decreasing solubilities in water (see Table 3), and the high and low recoveries within a set of SFE or PLE data are designated. The bold (high) and italic (low) values help to show the effects of water in extraction of pesticides with a wide range of polarity. The low recoveries within a data set occur more frequently to the left (less water content) at the top of the table (the more polar pesticides), and move to the right (higher water content) for the more non-polar pes-

Table 4
The effect of water–CF-1 ratio on average %recoveries (%R.S.D.), $n=2$, in SFE and PLE of the pesticides (**high** and *low* recoveries designated for each pesticide within each data set)

Pesticide	SFE					PLE				
	Dry	1:1	2:1	3:1	4:1[1]	Dry	1:1	2:1	3:1	4:1
Category A: Pesticides with increasing recoveries vs. increasing water–CF-1 ratio										
Imazalil	*1*[1]	14[1]	46 (1)	**54** (8)	31	*88* (3)	100 (2)	115 (5)	116 (0)	**121** (1)
Thiabendazole	ND	ND	2[1]	**42** (27)	ND	*36* (2)	87 (3)	**97** (3)	96 (0)	89 (2)
Category B: Pesticides with insignificant or minor differences in recoveries vs. water–CF-1 ratio										
Phosphamidon	84 (5)	**128** (18)	107 (8)	116 (5)	*67*	**109** (2)	104 (1)	**109** (6)	103 (1)	*96* (1)
Mevinphos	*73* (10)	**112** (19)	102 (8)	87 (2)	77	102 (2)	99 (2)	**105** (1)	96 (2)	*88* (2)
Dimethoate	91 (5)	**112** (4)	94 (14)	103 (10)	ND	102 (0)	101 (1)	**106** (6)	101 (1)	*94* (1)
Dichlorvos	*74* (3)	95 (18)	92 (10)	**96** (0)	86	94 (0)	*88* (0)	**95** (5)	91 (3)	91 (1)
Propoxur	*71* (4)	**90** (13)	85 (12)	84 (4)	*71*	**104** (0)	103 (0)	103 (5)	103 (1)	*100* (2)
o-Phenylphenol	*91* (5)	**112** (15)	102 (6)	92 (16)	112	**103** (1)	*98* (2)	102 (5)	99 (0)	100 (1)
Carbofuran	81 (5)	**96** (12)	90 (14)	84 (5)	*80*	103 (2)	100 (0)	**108** (5)	105 (1)	*99* (1)
Fenamiphos	*93* (1)	109 (19)	96 (1)	**119** (5)	94	100 (2)	*96* (2)	**105** (5)	103 (0)	102 (0)
Methidathion	96 (8)	**115** (16)	98 (8)	94 (8)	*78*	**118** (0)	102 (3)	109 (6)	102 (1)	*98* (0)
Myclobutanil	*68* (3)	82 (22)	80 (8)	**90** (10)	83	**110** (0)	*104* (0)	**110** (5)	107 (0)	107 (2)
Malathion	87 (17)	**106** (13)	87 (9)	93 (3)	*76*	**105** (1)	100 (1)	103 (5)	102 (1)	*98* (0)
Carbaryl	*85* (5)	**112** (18)	106 (6)	97 (3)	94	99 (2)	97 (1)	**103** (6)	96 (1)	*95* (4)
Chlorpropham	*76* (6)	85 (20)	83 (5)	78 (5)	**87**	**106** (1)	*97* (3)	101 (4)	100 (2)	101 (0)
Parathion-methyl	101 (16)	**120** (15)	106 (7)	99 (9)	*97*	**106** (0)	*96* (3)	100 (4)	101 (1)	*96* (2)
Diazinon	72 (14)	**76** (13)	64 (6)	*60* (2)	69	**109** (2)	100 (1)	106 (1)	*97* (1)	98 (1)
Atrazine	*79* (8)	**91** (14)	84 (11)	80 (4)	84	**102** (2)	100 (2)	101 (7)	**102** (2)	*97* (1)
Diphenylamine	83 (9)	92 (16)	85 (3)	*66* (17)	**93**	*89* (5)	104 (3)	**108** (5)	101 (0)	100 (4)
Parathion	107 (20)	**130** (12)	101 (10)	109 (9)	*83*	**103** (1)	97 (2)	101 (4)	96 (2)	*93* (3)
Phosmet	106 (18)	**115** (25)	100 (5)	108 (3)	*71*	**101** (1)	93 (0)	99 (3)	95 (2)	*89* (4)
Azinphos methyl	91 (7)	110 (28)	93 (2)	**127** (12)	*78*	**107** (1)	101 (2)	101 (4)	98 (2)	*93* (3)
Phorate	70 (11)	**75** (18)	*62* (0)	65 (15)	68	**110** (1)	99 (2)	104 (6)	96 (3)	*91* (1)
Disulfoton sulfone	*82* (22)	90 (1)	**101** (12)	94 (23)	96	**100** (1)	93 (2)	97 (5)	91 (1)	*85* (1)
Iprodione	81 (6)	90 (8)	81 (8)	**95** (0)	*77*	97 (3)	95 (3)	100 (3)	**104** (3)	*90* (2)
Dicloran	80 (20)	90 (5)	89 (11)	*66* (5)	**91**	**103** (2)	*95* (1)	97 (5)	97 (1)	97 (2)
Lindane	79 (13)	**85** (17)	81 (14)	*72* (0)	81	107 (0)	102 (1)	**109** (4)	101 (1)	*98* (0)
Phosalone	98 (2)	**104** (15)	82 (10)	80 (2)	*74*	**96** (1)	91 (3)	**96** (2)	86 (4)	*82* (4)
Vinclozolin	74 (7)	**84** (15)	75 (9)	*69* (1)	77	**111** (1)	103 (0)	110 (5)	105 (2)	*97* (3)
Dichlorobenzophenone	103 (13)	**109** (14)	92 (7)	*80* (1)	91	**107** (2)	104 (0)	**107** (4)	102 (1)	*99* (1)
Chorothalonil	107 (2)	124 (13)	**128** (18)	107 (18)	*82*	**100** (3)	91 (2)	95 (6)	95 (4)	*88* (3)
Category C: Pesticides with decreasing recoveries in SFE vs. increasing water–CF-1 ratio and minor differences in PLE										
Terbufos	80 (16)	**87** (10)	64 (4)	*36* (18)	62	**117** (0)	109 (3)	115 (4)	106 (2)	*101* (1)
Ethion	82 (17)	**83** (14)	51 (1)	*36* (5)	52	**104** (0)	97 (1)	103 (3)	94 (1)	*86* (2)
Chlorpyrifos	83 (15)	**90** (8)	57 (7)	*44* (15)	59	**107** (2)	103 (2)	105 (6)	96 (1)	*92* (6)
Dacthal	74 (17)	**80** (9)	67 (10)	*60* (1)	62	**108** (2)	100 (2)	103 (5)	95 (2)	*93* (2)
Pendimethalin	93 (19)	**100** (13)	58 (2)	*37* (6)	55	104 (1)	99 (2)	**107** (3)	100 (1)	*96* (2)
Trifluralin	**81** (17)	79 (13)	44 (2)	*22* (5)	48	**104** (1)	96 (1)	101 (6)	90 (0)	*87* (2)
Endosulfans	76 (13)	**80** (13)	60 (8)	58 (8)	*56*	**102** (1)	100 (1)	**102** (4)	96 (2)	*90* (4)
Methoxychlor	82 (2)	**89** (19)	51 (1)	*28* (20)	49	85 (1)	88 (1)	**93** (2)	84 (0)	*81* (4)
Quintozene	79 (19)	**86** (10)	65 (7)	*40* (20)	61	**102** (3)	98 (3)	98 (3)	93 (4)	*89* (3)
Aldrin	**78** (18)	**78** (11)	42 (1)	*19* (5)	46	**104** (0)	99 (2)	97 (5)	89 (1)	*85* (3)
Permethrins	**84** (14)	68 (5)	*35* (13)	59 (40)	40	**102** (1)	96 (2)	**102** (2)	92 (2)	*83* (4)
Fenvalerates	**86** (12)	70 (3)	*33* (20)	34 (30)	38	102 (1)	99 (1)	**107** (4)	96 (0)	*88* (4)
p,p'-DDE	**77** (16)	69 (10)	34 (8)	*24* (23)	44	**108** (1)	105 (0)	105 (4)	98 (2)	*91* (5)
o,p'-DDT	**80** (16)	74 (11)	37 (10)	*24* (18)	41	**104** 90)	100 (2)	103 (4)	94 (1)	*89* (5)

(*continued on p. 320*)

Table 4 (*continued*)

Pesticide	SFE					PLE				
	Dry	1:1	2:1	3:1	4:1[1]	Dry	1:1	2:1	3:1	4:1
Cypermethrin	**86** (9)	70 (7)	34 (16)	*32* (30)	41	**103** (0)	97 (1)	101 (3)	91 (1)	*84* (4)
Pentachlorobenzene	66 (13)	**68** (16)	48 (1)	*33* (13)	57	**109** (4)	93 (1)	87 (5)	78 (5)	*76* (2)
Hexachlorobenzene	**71** (18)	**71** (11)	47 (4)	*29* (0)	49	**108** (3)	100 (2)	98 (3)	90 (1)	*83* (6)
Category D: Pesticides with decreasing recoveries vs. increasing water–CF-1 ratio										
Methamidophos	31 (7)	**41** (67)	ND	ND	ND	90 (0)	**97** (0)	92 (6)	68 (3)	*51* (1)
Acephate	**78** (11)	58 (72)	ND	23 (63)	ND	**91** (2)	89 (3)	80 (6)	58 (5)	*36* (4)
Omethoate	38[1]	**58**[1]	ND	ND	ND	**100** (9)	**100** (3)	88 (9)	67 (10)	*36* (7)
Category E: Pesticides involved in degradation processes										
Disulfoton	**87** (21)	80 (17)	62 (3)	*46* (32)	68	**114** (2)	101 (9)	107 (6)	93 (3)	*84* (3)
Propargite	95 (17)	**99** (1)	51 (11)	*44* (11)	*44*	105 (4)	104 (2)	**108** (0)	88 (4)	*60* (1)
Captan	103 (8)	**113** (13)	83 (17)	102 (4)	*66*	**113** (0)	88 (5)	86 (7)	73 (3)	*43* (31)
Tetrahydrophthalimide	69 (2)	**121** (13)	85 (18)	54 (34)	*29*	*87* (1)	98 (3)	106 (5)	106 (1)	**109** (4)

Pesticides are listed in order of decreasing solubilities in water within each category.

ND=Not detected.

[1] Single replicate.

ticides. Conversely, the bold values have a general trend to the left as water solubilities decrease down the table. In PLE, the differences between the high and low recoveries were small, and the effect of water was negligible except for the most polar and non-polar pesticides. However, in SFE, the relationships between the polarity of a pesticide, water content in the matrix, and extraction efficiency were significant for many pesticides.

Fig. 1 shows the effect of pesticide solubility in water on SFE of dry and wet CF-1 matrices. The pesticide recoveries in Fig. 1 were normalized by dividing the recovery from the dry or wet matrix by the overall average SFE recovery for each pesticide.

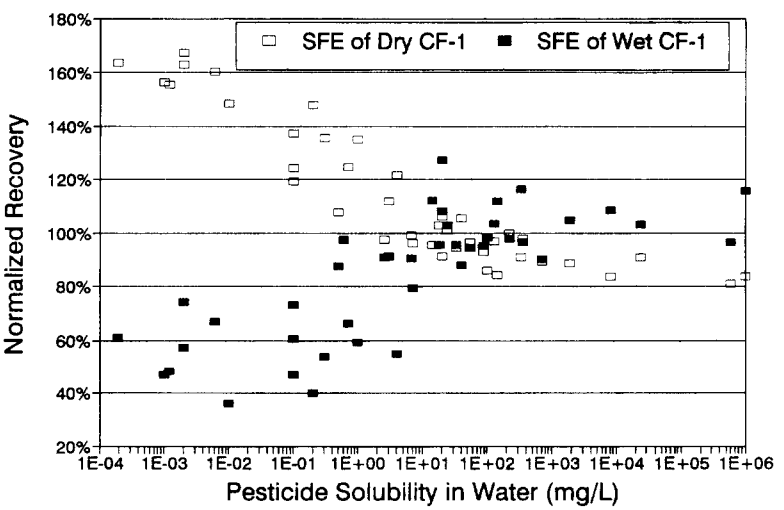

Fig. 1. The effect of solubility of pesticides in water on normalized SFE recoveries from dry CF-1 and (3:1) water–CF-1 (wet CF-1). Only pesticides from categories B and C (Table 4) with solubility data from Table 3 were included in the plot. Normalization was performed by dividing recovery from the dry or wet matrix by average overall recovery for each pesticide.

The pesticide solubility data were from Table 3 (lowest value was used when a range was given), and only pesticides in categories B and C (Table 4) with known solubilities were included in the graph. A clear trend of SFE extractability versus water solubility of the pesticides occurred which depended on the presence of water in the sample. For the most non-polar pesticides, a dry matrix gave higher recoveries in SFE, and a wet matrix slightly increased recoveries of the most polar pesticides. These aspects will be discussed in more detail below.

In Table 4, category A consists of two imidazole pesticides, imazalil and thiabendazole, which gave generally increasing recovery versus increasing water content in both SFE and PLE. These fungicides do not follow the general trend based on water solubility found with the other pesticides. Other organonitrogen pesticides, diphenylamine and tetrahydrophthalimide, were the only other compounds with lowest recovery from dry CF-1 in PLE, while iprodione (an imidizolidine), atrazine (a triazine) and myclobutanil (a triazole) had insignificant differences in recoveries versus water content in both SFE and PLE. The weak acid–base properties of thiabendazole (pK_a=4.73) and imazalil were the likely cause of the observed trend. These pesticides are not typically analyzed in a multiresidue GC scheme [11,14], and they give very broad peaks and high LOD with GC–ITD; separate clean-up and HPLC analysis of benzimidazoles is more commonly performed [15,16]. In single analyte methods, the imidazole pesticides are extracted with basic conditions into an immiscible solvent [17], or with acid conditions into water [18]. A reversed-phase (RP) HPLC method of these and other fungicides has been developed [19] that could be useful in an overall approach. Immunochemical analysis is another option [20]. Previously, a separate SFE (with HPLC analysis) method was developed for benzimidazoles [21], but we attempted to create a single multiresidue approach in this study.

Category B pesticides were not affected much by water content in either SFE or PLE. This group includes most of the organophosphates, carbamates and other moderately polar pesticides with solubilities in water from ≈1 mg/l to 1 kg/l. These pesticides are soluble in a wide range of solvents and generally do not provide difficulties in extraction. The only organochlorine pesticides in this group were chlorothalonil, lindane and 4,4′-dichlorobenzophenone (breakdown product of dicofol). These pesticides had solubilities in water in the transition region from category B to category C pesticides. A small difference in pesticide solubility in water can have a large effect on SFE in this region. Based on these results, increasing the solubility of a pesticide in water may improve SFE recoveries for transition pesticides in samples that contain water.

Category C contained the most non-polar pesticides in the mixture with solubilities in water from ≈2 μg/l to 5 mg/l. Pesticides in this group consisted of organochlorines, pyrethroids, dinitroanilines and the least polar organophosphates. These pesticides gave relatively minor differences in PLE recoveries, but a definite trend of decreasing recoveries versus increasing water content in CF-1 occurred. In PLE, the most likely cause of this effect was that water increased the polarity of the acetonitrile to the extent that the non-polar pesticides became less soluble in the extraction solvent, and recoveries decreased. This trend was much more apparent in the SFE results, but the cause of the effect was different because water content in supercritical CO_2 was the same (saturated) in all instances except for the dry CF-1. In SFE, the water acted as a barrier between the supercritical CO_2 and the water insoluble pesticides on the matrix surfaces. Pesticides in category C, although readily soluble in the non-polar supercritical CO_2, could not diffuse through the water to reach the extraction fluid, nor could the fluid penetrate the water to reach the pesticides in the CF-1 pores. If methylene chloride, hexane or other immiscible solvent was used in PLE, a similar situation occurs. On the other hand, pesticides in category B were likely dissolved in the water rather than precipitated in pores of the matrix, and could readily diffuse into the supercritical CO_2 phase as in a traditional liquid–liquid extraction.

The pesticides in category D (methamidophos, acephate and omethoate) are three of the most water soluble pesticides in the mixture. These phosphoro(amido)thioate pesticides are difficult, even with traditional methods of multiresidue extraction using liquid–liquid partitioning and/or solid-phase clean-up [15]. Due to their high polarity, the pesticides are only partially transferred into the organic layer in

liquid–liquid partitioning. In PLE, the cause of the observed effect was related in part to the salt water–acetonitrile partitioning step. As the water phase (saturated with NaCl) volume increased in each partition, the amount of pesticide in the acetonitrile phase decreased. Furthermore, PLE gave a fixed volume of ≈22 ml per extraction, independent of water content in the sample, which meant that the volume of acetonitrile decreased as water volume increased. However, this effect alone cannot account for the observed decrease because the distribution coefficient was not constant versus volume in this case. Matrix interactions of CF-1 with these pesticides, which depended on the amount of water present, were the probable cause of the lower recoveries, albeit to a lesser extent in PLE than SFE, as discussed below.

In SFE, the results of pesticides in category D were partially a result of incomplete distribution of the pesticides from the aqueous phase into the supercritical CO_2, and partially a result of matrix interactions. As in PLE, recoveries decreased as more water was added in the vessel. However, other pesticides with equally high water solubility, such as phosphamidon and mevinphos, did not exhibit the same effect as category D pesticides. The different results for these pesticides of similar polarity indicates that pesticide interactions with the matrix occurred. Oostdyk et al. [22] suggested that SiOH in soil formed hydrogen bonds with amino groups. CF-1 contains many hydroxyl groups according to the manufacturer, and hydrogen bonding interactions form the most likely explanation for the observed effect in this case. Methamidophos is a primary amide, and acephate and omethoate are secondary amides.

The category E pesticides, disulfoton, captan and propargite, are known to degrade during extraction [3,8], and they are included in this separate category because their results do not conform to results of pesticides in categories A–D with similar water solubilities. These pesticides appear to conform to patterns of category C or D, which may be the case, but degradation is the more likely explanation for the results. Tetrahydrophthalimide, a degradation product of captan, is included in category E because its results are also suspect. Tetrahydrophthalimide could belong in category A based on PLE results, or category D based on SFE results, but the likelihood of captan degradation placed tetrahydrophthalimide in category E. Disulfoton sulfone, a degradation product (along with disulfoton sulfoxide) of disulfoton, conformed to the pattern of category B pesticides in SFE and PLE. The elevated extraction temperature, presence of oxygen and longer storage times involved in the extraction and analysis could be the source of the decreasing recoveries of category E pesticides versus increasing water content. Complications due to degradation preclude conclusions that can be made about these pesticides based on apparent results.

All pesticides in PLE gave recoveries ≥80% in (1:1) and (2:1) water–CF-1 ratios. Dry CF-1 gave recoveries ≥87% except for thiabendazole, but in the extraction of wet samples, dry material cannot be used (lyophilization is time-consuming and loses volatile pesticides [23]). Water–CF-1 ratios of (3:1) and (4:1) gave low recoveries of category D and a few other pesticides. In SFE, the effect of water was more pronounced, and no single water–CF-1 ratio gave high recoveries for all pesticides. A (1:1) water–CF-1 ratio was the best compromise conditions for extraction; only thiabendazole was not recovered at all. Tomato–CF-1 ratios of (1:1) and (2:1) were chosen for further testing in SFE and PLE.

3.3. Recovery of pesticides from tomato–CF-1

Table 5 presents SFE and PLE recoveries, R.S.D. and LOD of the pesticides in (1:1) and (2:1) tomato–CF-1 samples fortified with 10 μl spiking solution per g tomato (Table 3 provides pesticide concentrations of the spike solution). The pesticides are listed in order of increasing average LOD for (1:1) tomato–CF-1 in PLE. The LOD (ng/g in tomato) in Table 5 account for recoveries and were calculated from the average of individual LOD determined from calibration standards equivalent to 25%, 50% and 100% recoveries in each matrix. The on-column sample injection amounts were 1.67 mg, 2.5 mg, 1 mg and 2 mg of tomato for (1:1, SFE), (2:1, SFE), (1:1, PLE) and (2:1, PLE) tomato–CF-1 ratios, respectively. The lowest LOD for each pesticide within a data set appears in bold type.

The effect of matrix interferences were often

Table 5
Average %recoveries (%R.S.D.) and LOD for the pesticides [listed in order of increasing LOD in PLE of (1:1) tomato–CF-1] in fortified (1:1) and (2:1) tomato–CF-1 samples extracted with SFE ($n=3$) and PLE ($n=2$)

Pesticide	SFE				PLE			
	(1:1) Tomato–CF-1		(2:1) Tomato–CF-1		(1:1) Tomato–CF-1		(2:1) Tomato–CF-1	
	%Recovery (%R.S.D.)	LOD (ng/g)	%Recovery (%R.S.D.)	LOD (ng/g)	%Recovery (%R.S.D.)	LOD (ng/g)	%Recovery (%R.S.D.)	LOD (ng/g)
Trifluralin	66 (9)	**0.3**	25 (2)	0.4	94 (4)	0.5	87 (2)	0.5
Pendimethalin	82 (5)	**0.4**	40 (10)	**0.4**	105 (1)	0.7	100 (1)	**0.4**
Diazinon	94 (2)	1	73 (4)	1	98 (1)	1	88 (6)	**0.4**
Ethion	78 (4)	**0.6**	38 (2)	**0.6**	101 (1)	2	94 (1)	1
Malathion	114 (1)	4	77 (3)	**2**	108 (8)	**2**	48 (11)	4
Diphenylamine	95 (2)	2	68 (4)	**1**	117 (9)	2	98 (8)	**1**
Parathion	101 (4)	1	78 (1)	**0.7**	104 (1)	3	95 (2)	2
Methoxychlor	73 (13)	2	41 (8)	2	117 (0)	3	134 (23)	**1**
o-Phenylphenol	106 (4)	**0.6**	85 (4)	2	104 (9)	3	97 (2)	2
Methidathion	104 (4)	**2**	88 (3)	**2**	97 (0)	3	97 (2)	7
p,p'-DDE	61 (10)	3	24 (2)	**2**	112 (3)	3	96 (2)	**2**
Hexachlorobenzene	77 (4)	**1**	42 (5)	**1**	84 (3)	3	81 (2)	2
cis-Permethrin	57 (7)	**1**	20 (8)	4	103 (2)	3	95 (0)	2
trans-Permethrin	57 (5)	**2**	21 (8)	4	103 (1)	3	92 (3)	3
Mevinphos	92 (5)	**1**	80 (2)	**1**	92 (2)	3	86 (4)	2
Parathion-methyl	104 (3)	1	92 (3)	**0.8**	98 (0)	3	96 (5)	3
o,p'-DDT	65 (8)	**2**	24 (9)	**2**	102 (3)	3	89 (3)	**2**
Pentachlorobenzene	70 (2)	**2**	46 (1)	**2**	69 (1)	4	73 (5)	**2**
Terbufos	87 (4)	**0.6**	54 (3)	0.8	97 (1)	4	94 (6)	2
Carbofuran	99 (3)	3	90 (4)	**0.8**	101 (2)	4	94 (2)	6
Phorate	91 (2)	1	72 (5)	**0.6**	86 (1)	5	87 (5)	2
Vinclozolin	99 (1)	**1**	84 (2)	2	104 (0)	5	99 (7)	4
Dacthal	98 (5)	**0.5**	71 (3)	0.9	108 (5)	5	94 (5)	5
Chorothalonil	59 (72)	7	72 (11)	**3**	98 (2)	7	83 (10)	6
Propoxur	101 (3)	**1**	87 (2)	2	110 (6)	7	105 (3)	2
Dicloran	99 (3)	4	84 (5)	**3**	96 (4)	7	93 (2)	6
Phosalone	104 (8)	5	75 (8)	**2**	118 (1)	8	110 (3)	6
Dichlorvos	91 (5)	**2**	73 (5)	3	55 (5)	8	47 (3)	7
Quintozene	92 (3)	**3**	57 (1)	4	92 (1)	9	88 (0)	6
Chlorpyrifos	85 (4)	**1**	43 (3)	2	102 (11)	9	88 (3)	5
Fenvalerate	58 (8)	**4**	20 (43)	9	105 (2)	10	97 (2)	6
Esfenvalerate	60 (7)	6	20 (49)	13	104 (2)	10	100 (3)	**5**
Disulfoton sulfone	124 (4)	21	96 (4)	**6**	110 (1)	12	97 (3)	17
Phosmet	103 (3)	**2**	95 (2)	**2**	85 (12)	12	89 (6)	9
Atrazine	113 (8)	**2**	91 (1)	**2**	115 (1)	13	92 (1)	6
Dichlorobenzophenone	91 (1)	7	67 (3)	**1**	105 (2)	14	97 (6)	8
Chlorpropham	102 (4)	2	83 (3)	**1**	108 (3)	14	93 (10)	4
Phosphamidon	99 (6)	4	87 (5)	**3**	106 (3)	15	96 (8)	12
Myclobutanil	103 (2)	9	91 (5)	9	109 (1)	15	100 (2)	**6**
Endosulfan II	95 (5)	9	66 (2)	**6**	105 (2)	16	104 (6)	14
Aldrin	64 (5)	**9**	27 (5)	10	104 (3)	18	94 (3)	11
Fenamiphos	84 (3)	4	78 (15)	**2**	105 (5)	18	90 (2)	9
Methamidophos	7 (12)	150	3 (83)	180	95 (8)	20	63 (5)	**13**
Propargite	72 (3)	16	33 (24)	**11**	95 (10)	22	81 (0)	19
Dimethoate	99 (4)	23	77 (9)	**6**	98 (3)	23	95 (4)	17

(*continued on p. 324*)

Table 5. (*continued*)

Pesticide	SFE				PLE			
	(1:1) Tomato–CF-1		(2:1) Tomato–CF-1		(1:1) Tomato–CF-1		(2:1) Tomato–CF-1	
	%Recovery (%R.S.D.)	LOD (ng/g)	%Recovery (%R.S.D.)	LOD (ng/g)	%Recovery (%R.S.D.)	LOD (ng/g)	%Recovery (%R.S.D.)	LOD (ng/g)
Endosulfan I	88 (6)	14	50 (3)	**9**	101 (0)	25	81 (4)	34
Iprodione	104 (2)	6	90 (1)	**3**	102 (11)	28	85 (2)	25
Captan	33 (30)	29	10 (158)	**22**	49 (11)	31	12 (17)	140
Carbaryl	101 (3)	3	89 (5)	**2**	93 (3)	35	95 (1)	20
Tetrahydrophthalimide	130 (8)	**2**	103 (5)	**2**	104 (5)	38	112 (5)	41
Disulfoton	80 (8)	5	64 (11)	**3**	79 (13)	40	72 (1)	27
Cypermethrin	59 (7)	**20**	22 (155)	33	100 (7)	45	92 (1)	33
Thiabendazole	4 (77)	>1000	7 (1083)	>1000	109 (5)	64	100 (2)	**15**
Omethoate	14 (29)	820	5 (142)	140	89 (7)	66	71 (13)	**23**
Lindane	101 (3)	32	81 (0)	**15**	104 (2)	82	92 (4)	52
Acephate	7 (2)	76	4 (90)	70	88 (1)	130	75 (9)	**14**
Azinphos methyl	110 (6)	29	99 (17)	**11**	102 (2)	130	78 (12)	62
Imazalil	41 (27)	770	32 (457)	600	109 (3)	220	109 (3)	**140**

apparent in the LOD. In cases that the *S/N* ratio of a pesticide was limited by matrix, the injection of more sample did not alter the LOD. If matrix was not the limiting factor, the LOD decreased roughly in proportion to the amount of additional sample injected. For example, trifluralin was limited by matrix in PLE because the LOD of (2:1) tomato–CF-1 would have been half that of (1:1) tomato–CF-1 (with similar recovery) if matrix was not limiting, such as in the case of pendimethalin. In SFE, detection of trifluralin and pendimethalin were not limited by matrix because (2:1) tomato–CF-1 gave lower LOD when corrected for recoveries. More analytes were affected by matrix in PLE than SFE using GC–ITD analysis. Pesticides with significantly higher LOD in PLE than SFE due to matrix include iprodione, tetrahydrophthalimide, carbaryl, azinphos methyl and endosulfan. SFE gave higher LOD in cases of poor recovery, which include methamidophos, acephate, omethoate, imazalil and thiabendazole, but not due to matrix. Quantitation masses were altered in PLE in some cases (see Table 3) to avoid matrix interferants, but usually at the expense of *S/N*. However, matrix was not always the limiting factor in LOD results which were independent of amount injected; *S/N* of dacthal in both SFE and PLE was limited by the presence of aldrin in the pesticide mixture.

Fig. 2 presents a comparison of GC–ITD total ion chromatograms of blank (1:1) and (2:1) tomato–CF-1 SFE and PLE extracts scaled in equal proportions to the intensity of the internal standard peaks. All extracts contained many matrix components, several of which were the same, but a higher baseline occurred in PLE. Several broad matrix peaks appeared in the PLE extracts that increased LOD of co-eluting pesticides, such as iprodione, and endosulfans. Fig. 3 shows this effect for endosulfans in matrix-based calibration standards equivalent to 50% recoveries (0.15 μg/g for endosulfans in tomato). The 241 *m/z* was dropped from quantitation of endosulfan I in PLE, but interferants were still limiting in detection.

An interesting effect of the higher water content in SFE with (2:1) tomato–CF-1 was the reduction of certain matrix components (Fig. 3b) in parallel with the reduction in recoveries of non-polar pesticides. LOD of many pesticides were not affected, or even improved, despite the lower recoveries in this case. For pesticides with extraction efficiencies that were unaffected by water content, such as carbofuran, potential interferants can be reduced and more sample can be extracted/injected by increasing the sample–drying agent ratio in SFE.

Despite the lower recoveries for many compounds, SFE gave lower LOD than PLE for several pesticides mainly due to matrix interferants in PLE. The higher degree of selectivity in SFE allows direct injection of

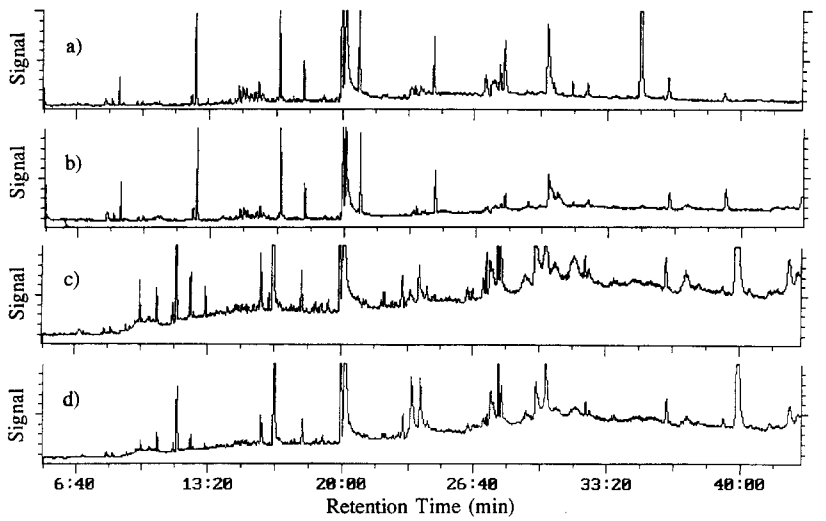

Fig. 2. GC–ITD total ion chromatograms of blank tomato–CF-1 extracts normalized to scales 50 times higher than average peak height of the internal standards: (a) SFE of (1:1) tomato–CF-1; (b) SFE of (2:1) tomato–CF-1; (c) PLE of (1:1) tomato–CF-1 and (d) PLE of (2:1) tomato–CF-1.

tomato extracts in routine analysis. Whether routine analysis of the PLE extracts would require clean-up is a matter of debate. Cairns et al. [24] present GC–ITD chromatograms of tomato and other sample extracts from the "Luke II" method which demonstrate the effect of clean-up of acetone-based extracts. However, similar extracts are acceptable without clean-up based on the Dutch multiresidue

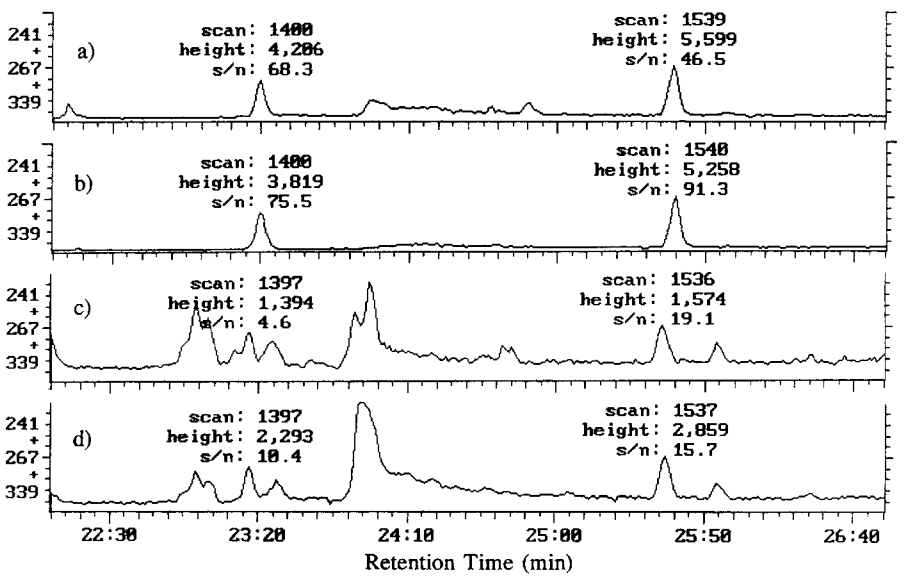

Fig. 3. GC–ITD chromatograms of 50% recovery standards in matrix. Quantitation masses of 241+267+339 u for 0.15 μg/g in tomato for endosulfan I (left) and endosulfan II (right): (a) (1:1) tomato–CF-1 SFE extract (1.67 mg tomato injected); (b) (2:1) tomato–CF-1 SFE extract (2.5 mg tomato injected); (c) (1:1) tomato–CF-1 PLE extract (1 mg tomato injected) and (d) (2:1) tomato–CF-1 PLE extract (2 mg tomato injected).

method, which also relies mainly on GC–ITD analysis [25]. Liao et al. [26] using a rapid extraction method similar to this PLE method, also concluded that clean-up for GC–MSD analysis is often unnecessary.

The same trends of water content in CF-1 versus recoveries in SFE and PLE (Table 4) occurred in the tomato–CF-1 (Table 5). In SFE, the polar pesticides, methamidophos, acephate, omethoate, thiabendazole and imazalil gave low recoveries (3–41%), and nonpolar pesticides gave decreasing recoveries versus increasing water content. In PLE, recoveries of nearly all pesticides were >80% in both (1:1) and (2:1) tomato–CF-1 ratios. The only pesticides with recoveries <80% degraded (captan, disulfoton), volatilized during the evaporation step (dichlorvos and pentachlorobenzene), or were affected by the higher water content in (2:1) tomato–CF-1 (acephate, methamidophos and omethoate). Malathion and azinphos methyl gave lower recovery in (2:1) tomato–CF-1 as a result of poor quantitation due to large matrix interferants.

4. Conclusions

This study determined that CF-1 is not as useful as a drying agent for wet samples as Hydromatrix. Although the cellulose powder strongly retained water, in practice, it costs too much and has a too fluffy consistency. Furthermore, CF-1 gave a stronger effect than Hydromatrix on the retention of certain pesticides (presumably caused by hydroxyl groups) due to the effects of water in the sample. This enhanced effect, however, gave conditions for interesting experimentation to compare SFE with liquid-based extraction of analytes having a wide range of polarity. The higher degree of selectivity in SFE than PLE was demonstrated in experiments to measure the effects of water and in determinations of the pesticides in tomato. The dependence of analyte solubility in water on SFE recovery in a wet matrix was clearly shown in these experiments. PLE gave higher recoveries for a wide range of pesticides with a single set of conditions, and extraction was very rapid, but manual post-extraction steps (separation of water and solvent evaporation) were required before analysis. Whether PLE extracts require further clean-up depends on the application, the laboratory's quality control practices and the analyst's judgment. SFE extracts can typically be injected in GC–ITD routinely without post-extraction steps or additional clean-up. The trade-off for the increased selectivity in SFE is reduced recoveries of some pesticides. With SFE, current options in extraction of diverse pesticides are to use two or more sets of conditions to recover the pesticides, or to perform separate methods (e.g., immunochemical analysis) for those pesticides not recovered in SFE.

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